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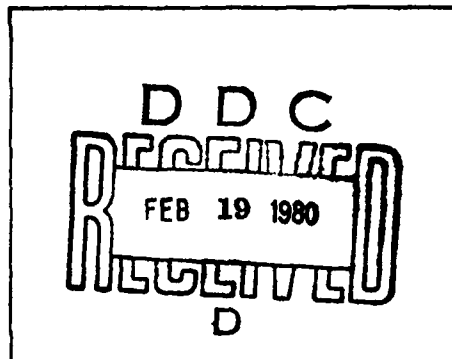
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Ni AND Co CONTENTS

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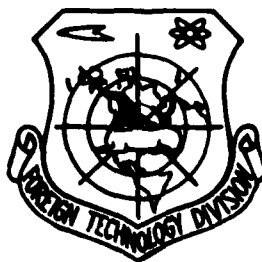
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An Investigation of A Maraging Steel
With Lower Ni and Co Contents

By

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Shen Hui-wang   Lo Li-keng   Sung Wei-shun
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Abstract

Our experiments indicate that 12Ni maraging steel containing Mn and

Cr and with lower Ni and Co contents maintains high strength and toughness.

Observing the precipitation phases after aging and the dislocation

configurations and analysizing the easy cross-slip behavior of dislocations,

we try to discuss the results on an assumption that the hexagonal close-

packed phases were precipitated along the stacking fault zone of the

dislocation lines. In order to predict the stability and solubility of high-

temperature austenite in maraging steels, a criterion has been suggested

from the point of view of average electron concentration per atom of the alloy.

The criterion wi'l be found helpful for rational alloying of maraging steels

with lower Ni and Co contents.

In a previous article,[1] the authors, based on the characteristics of

the dislocation structure in 18Ni maraging steel, the form and structure of

the precipitation phases along the dislocation lines, the orientational

relationship of the precipitation phases and the matrix and some other

phenomena observed in experiments, have suggested an assumption that the

fault zone along the dislocation lines in a body-centred cubic martensite

matrix, because of the existence of hexagonal close-packed lattice structure,

is helpful for the nucleation of hexagonal close-packed precipitation phases.

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This assumption can explain the fact that in aging, the hexagonal close-packed phases Ni_3Ti and Ni_3Mo precipitated out along the orientational pure spiral dislocation lines of <111> will be good for energy. Using this assumption, some other phenomena observed in experiments can be explained, and from the structural point of view, it can explain the interaction of Co-Mo as well.

On this basis, this article is attempting, by using transmission electron microscope to make further investigation of the precipitation phases and dislocation configurations after aging of 12Ni maraging steel of which Ni and Co are partially replaced with Mn and Cr; to analyze the characteristics of the cross-slip behavior of dislocations; to apply the method used in the study of high-temperature alloy of using the average electron hole number or average electron concentration successfully to predict the stability and solubility of austenite to maraging steels; and finally to suggest a criterion of average electron concentration. Through these studies, we intend to suggest some useful knowledge for rational alloying of maraging steels with lower Ni and Co contents.

1. Criterion of Average Electron Concentration

One important prerequisite for super-high strength and high toughness of 18Ni maraging steel is that during the high-temperature solid solution treatment, a full austenite structure containing great amount of such strengthening elements as Mo, Ti and others can be obtained so that a supersaturated full martensite will come out after cooling. But, if such strengthening elements as Mo, Ti, Al, V, and Si are added too much, the result will be just the opposite. Because the solubility of austenite matrix is

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limited, along austenite crystal boundary or in the crystal there will be great amount of undissolved second phases, which are not only useless for age strengthening, when break occurs, they often become the source of plastic cavity and damage the toughness. On the other hand, all these strengthening elements can help to close the gamma zone, and after being dissolved into the matrix as the solid solution temperature is increased, they always help to form delta iron of high temperature ferrite. So after cooling, there will be no full martensite structure. Therefore, the criterion of an appropriate amount of these strengthening elements will be determined by the stability of the austenitic base at high temperature and the solubility of the strengthening elements.

In the study of high temperature alloys, someone[2] has, based on phase analyses and state diagrams, suggested a criterion of the average electron concentration of alloys of Ni and Co base. By using average electron hole number $\bar{N}_v$ per atom of d shell of an alloy or the average electron number $\bar{N}_{spd}$ of the outer shell (namely spd shell), the stability of austenitic base at high temperature and the solubility of strengthening elements Mo and Ti can be determined. The formula of average outer shell electron number $\bar{N}^*_{spd}$ which, as has been concluded in some writings, at a temperature range of 800°C—1200°C, can guarantee the stability or not over saturated (solution limit) of austenite structure, will be:

For alloy of Ni base,

$$N^*_{spd} = 8.20 + 0.2\left(\frac{1200 - T}{100}\right)$$

For alloy of Co base,

$$\overline{N}_{spd}^{*} = 7.95 + 0.16\left(\frac{1200 - T}{100}\right)$$

T stands for Celsius temperature. This criterion can be expressed by the average electron hole number $\overline{N}_v$. Because the electron number filled in d shell is 10, the electron number of the conduction band is 0.66, so the relationship between the electron hole number N_v of d shell and the electron number N_{spd} of spd shell is:

$$N_v = 10 + 0.66 - N_{spd} = 10.66 - N_{spd}$$

The relationship between high temperature alloys of Ni base and Co base mentioned above can be extended to alloy of ferric base. According to the conclusions of investigating ferric based alloys of different compositions and maraging steels and the result of analysizing X-ray high temperature diffraction phases, we know that the average electron concentration limit for austenite structural stability or saturation of ferric based alloys at a temperature range of 800°C–1200°C is:

$$\overline{N}_{spd} = 7.75 + 0.10\left(\frac{1200 - T}{100}\right) \qquad (1)$$

Here T stands for Celsius temperature. The criterion of stability mentioned above, if expressed by using average electron hole number, will be:

$$\overline{N}_v = 2.91 - 0.10\left(\frac{1200 - T}{100}\right) \qquad (2)$$

Table 1 shows electron number N_{spd} of spd shell and electron hole number N_v of d shell outside the atomic inertia gas nucleus of various alloy elements. It must be pointed out that Mo and Cr of which the amount in an alloy is usually large belong to the same family in periodic table, so they

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should have same N_{spd} (family number) value. But due to the fact that the atomic size of Mo is obviously larger than the average atomic radius of Fe, Ni and Co, the solubility in austenite is therefore smaller than Cr. Because of this kind of atomic size effect, the effective N_{spd} value of Mo in the Table should be set as 2 in order to be in accordance with the experiment result of solution limit, and the corresponding effective value N_v of electron hole number of d shell should be 8.66. Although other elements such as V, Ti and Al also have the interference of atomic size effect, it is usually neglected because the contents of them in an alloy are insignificant.

Based on formula (1), it is possible to predict whether a designed alloy composition can guarantee to have full austenite structure in complete solid solution at high temperature. For instance, to guarantee a full austenite structure under 900°C, the average electron concentration of the alloy is required to be:

$$N_{spd} \geq 7.75 + 0.1\left(\frac{1200 - 900}{100}\right) = 8.05$$

Table 1

Alloy elements	Ni	Co	Fe	Mn	Cr	V (Nb,Ta)	Ti (Zr,Si)	Al	Mo(W)
N_{spd}	10	9	8	7	6	5	4	3	2
N_v	0.66	1.71	2.66	3.66	4.66	5.66	6.66	7.66	8.66

In Table 2, there are results of actual test of high temperature X-ray diffraction of some alloys. It can be seen that when the average electron concentration $\bar{N}_{spd}$ is lower than the boundary value $\bar{N}^*_{spd}$ given in formula (1), under the state of high temperature solid solution, there will be a great amount of delta-iron but no full austenite structure. In the remaining delta-iron zones after cooling, there is no high dislocation density and

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substructure, so after aging, there will be no gain in high strength and high toughness. It should be pointed out that in the low solid solution temperature zone (for example $800^\circ C-900^\circ C$), if the alloy electron concentration is insufficient (namely $\bar{N}_{spd} < N^*_{spd}$), there can be at the same time delta-iron zone and great amount of second phases of metal compounds that are not dissolved (such as Fe_2Mo) or there is only one of them. The concrete will be determined by the free energy of delta-iron and metal compounds. Neither great amount of metal compounds nor delta-iron is good for the strength and toughness of maraging steel. So the criterion of average electron concentration mentioned above is a useful one for designing and adjusting alloy compositions.

Table 2

| Furnace No. | Alloy Compositions | | | | | | | | N_{spd} | X-ray high temperature diffraction and phase observation |
	Ni	Mn	Co	Mo	Ti	Al	V	Other		
A		11.7		4.05				0.78Si	7.65	900°C 845%δ Fe, 1000°C 855%δ Fe
B		7.85		3.95		1.89		2.11Cu	7.60	850-900°C δ Fe great amount of delta-iron
C	7.94	5.59		2.48	0.10	0.29	0.29	0.17Nb	7.94	800-1000°C δ Fe from phase
D	3.88	9.83		1.95		0.57	0.25	0.20Nb	7.90	800-1000°C δ Fe observation
F	6.46	3.01	4.52	4.35	0.17	0.32	0.34		8.08	850°C full austenite

In the study of reducing Ni and Co in maraging steels, Mn and Cr which are of low electron concentration are often used to substitute for Ni and Co which are of high electron concentration, and consequently the average electron concentration $\bar{N}_{spd}$ of the alloy becomes low and the stability and solubility of austenitic base under high temperature also become low. Viewed from the angle of electron concentration criterion, partial increase of strengthening elements Mn and Cr, which are of low electron concentration, often does not have the expected effect, and on the contrary, it can damage the total toughness. Then the amount of strengthening elements should be

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reasonably reduced and elements (such as Ti), which are of higher

strengthening effect, should be counted on more or some other strengthening
                              should be put into consideration.
means which does not depend on metal compounds. For instance, in the following

we shall discuss the possibility of using high dispersion reversed austenite

strengthening.

2. The Characteristics of the Easy Cross-slip Behavior of Dislocation lines of Fe-Ni Martensite Matrix

Someone believes that the main reason that Fe-Ni martensite matrix has

higher toughness is due to the result that Ni helps to increase the fault

energy of the alloy and the width of dislocation becomes narrower, so cross-

slip becomes easy to take place. If this is the case, the toughness will be

damaged when Co which can lower fault energy is added or especially when

Mn and Cr which can noticeably lower fault energy are used to substitute for

Ni and Co. But our experiment results indicate otherwise. As shown in Figure 1,

in our laboratory experiments of 12Ni maraging steel in which Mn 1.5% and

Cr 3% are used to substitute for Ni 6% and Co 5%, the outcome shows a

combination of super-strength and high toughness, $\sigma_b = 175-180 kg/mm^2$ and

$K_{1c} = 320-420 kg/mm^{-3/2}$. It thereby becomes known that the toughness of

Fe-Ni martensite matrix is not entirely determined by the width of dislocation.

The cross-slip is indeed a guarantee that the body-centred cubic delta-

iron will not have cold-short crack and that it 's a good deformation

control when the cold-short temperature is lowered. But the relationship

between cross-slip of spread dislocation and fault energy of face-centred

cubic austenite, as mentioned above, cannot be simply applied to body-centred

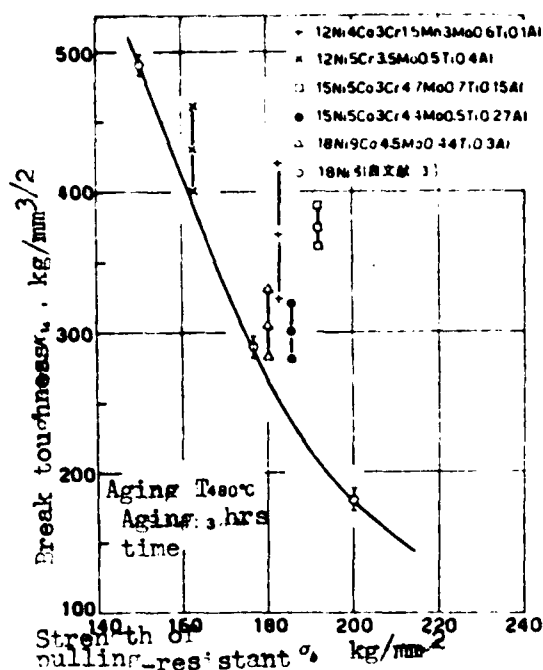cubic martensite under plastic state. In Fe-Ni martensite, when the

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Figure 1 The level of break toughness
and strength of maraging steel
containing Mn-Cr and with low
Ni-Co contents

Bu's vector* of a tilted dislocation is $\frac{a}{6}(11\bar{1})$ and its cross-slip is from (112) to ($2\bar{1}1$) or ($\bar{1}12$), there cannot be any press-bar dislocation. Because a full dislocation of which the fault energy becomes wide because it has been lowered, will not necessarily be something like in austenite that must become a pressed bunch before it $\underset{\wedge}{\text{becomes}}$ cross-slip, so when such elements as Co, Cr and Mn which can lower fault energy are added, it will not block cross-slip and will not damage the toughness either.

In theory, there is still another spreading dislocation configuration which can block the cross-slip of the spiral dislocation in a body-centred cubic metal, but in experiments, such a configuration has so far never been seen. In our laboratory, from the sample of 18Ni19Co maraging steel, we saw the traces of cross-slip of spreading dislocations under the effect of electron beam, as shown in Figure 2. The curve-lined traces pointed by the arrow are the complements to dislocation lines or spreading dislocation lines observed in experiment. They are exposed traces left over when the cross-

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* Bu's is a Chinese transliteration. It may be a short form of Burgers

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slip of dislocation was in movement. They are different from the straight-lined traces seen in austenite stainless steel. These curve-lined traces indicate that the cross-slip is continuous. We use electronic microscope to make further observation of the deformation structure of 18Ni maraging steel. Figure 3 shows its typical picture. We can see many wave-like cross-slip terraces. The wave-like slip lines indicate that cross-slip can occur anywhere, especially along the large grain precipitation phases, deeper traces of wave-like slip terraces can be seen. This evidences that the dislocation lines through cross-slip will go around large grain precipitation phases. So it is not easy in front of the large grain precipitation phases to produce high dislocation deposit stress which can cause crack along precipitation phase or phase boundary in early deformation. Certainly, the deep cross-slip terraces mean that when the dislocation lines are passing around the large grain precipitation phases, an adaptive concentration occurs on the terrace. This can cause crack in late deformation. So the concentration of large grain precipitation phases on crystal boundary or twin crystal boundary should be avioded. In short, from our observation in experiments, we know that it is easy to have cross-slip of dislocation lines in Fe-Ni martensite matrix, and the distribution of slip lines and deformation in the matrix is therefore relatively homogeneous. This is the reason why the toughness of maraging steel is high.

Because of the characteristics of cross-slip behavior of the dislocation lines in Fe-Ni maraging steel, it becomes possible to use Mn and Cr which can lower fault energy to substitute for Ni and Co. In Fe-Mn and Fe-Co, there are hexagonal close-packed phase zones, so within a range of middle or low temperature, the fault zone of martensite dislocation lines can be spread

and stabilized. This fault zone is also a hexagonal close-packed lattice zone. Thus when Mn is added to maraging steel, it can not only substitute for Ni by a ratio of 1:2.5 to lower M point so as to guarantee the forming of martensite structure in large pieces but also can partially substitute for Co to stabilize the fault zone of dislocation lines. Furthermore, it can partially take the place of interaction of Co-Mo to guarantee a combination of high strength and high toughness. In a series of Fe-Ni-Cr, Cr has the same function. This can be used to explain the fact as shown in Figure 1 that in maraging steel, using Mn and Cr to substitute for Ni and Co can result in super-strength and high toughness.

5. Discussion

5.1 The Control and Significance of the Precipitation on Dislocation Lines

On the matrix of body-centred cubic martensite are formed hexagonal close-packed precipitation phases of different structure but not body-centred cubic prolific phases of similar structure. Although it is different with the homogeneous iso-lattice precipitation phase control of high temperature alloy gamma', it gains high dispersity. As it can be seen in maraging steel, a long pre-precipitation zone is formed on the spiral dislocation lines which orientate along $\langle 111 \rangle$. For explaing this phenomenon, we , in a previous article, (1) suggested an assumption that in the fault layer of dislocation lines in the matrix of body-centred cubic martensite, there is a hexagonal close-packed lattice zone. Figure 8 is a diagram of the formation and structure of the assumed hexagonal close-packed lattice zone in the fault layer. The Figure shows the orientation relationship in the matrix used by reversed austenite and Ni_3Mo and Ni_3Ti which are nucleated according to this model. It must be

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pointed out that this model does not require a large fault width. According to the analyses of the experiment results in the previous article[1] and this one, this model at least can be satisfactorily used to explain the following experiment phenomena in maraging steels.

(1) The action of Co in stabilizing dislocation lines, and the difference of action of Mn, Cr and Co which can lower fault energy.

(2) The interaction of Co-Mo.

(3) The precipitation control along the spiral dislocation line.

(4) Why the stable phases precipitated on the dislocation lines are always hexagonal close-packed Ni_3Ti and Ni_3Mo (Fe_2Mo is also hexagonal and the reversed austenite can also be regarded as hexagonal close-packed lattice with fault), and not body-centred cubic prolific phases which are of similar structure with matrix.

(5) The orientation relationship of Ni_3Ti, Ni_3Mo, the reversed austenite and martensite.

(6) The space-lattice precipitation structure formed along four directions of $<111>$ type.

(7) Why the strengthening effect of Ti and Mo which can form hexagonal close-packed phases Ni_3Ti and Ni_3Mo is the highest and the damage of toughness is the least.

5.2 The Relationship of Aging Precipitation Phase and Temper Brittleness

18Ni19Co maraging steel at lower temperature ($<420°C$) and after a short time aging will have a certain degree of brittleness. But after a treatment of normal aging temperature and time, following the separation of precipitation phases and the improvement of strength, the toughness will be accordingly promoted. In some writings,[6] such a disappearance of brittleness is often

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attributed to the forming of reversed austenite. As indicated in article (~),

in the simply Fe-12Ni-0.25 Mn alloy steel, which has no Ni_3Ti, Ni_3Mo and

Fe_2Mo hexagonal precipitation phases, this kind of brittleness stands for

typical temper brittleness. Some cracks are breaks along the original

Figure 8 (a) In a body-centred cubic structure, when fault thickness of
           [111] spreads into a four-layer atomic face, this is a diagram
           of hexagonal close-packed lattice formed in fault zone. Notice
           the changes in the interactions among the close-packed atoms and
           transportation of atoms in the lower layer. "o" shows the position
           of upper layer atoms and "." the position of lower layer atoms.

     (b) A three-dimensional diagram of the spread dislocation and
           fault zone shown in Figure 8 (a).

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austenite crystal boundary. This kind of brittleness is usually regarded as a result of Sb, P, Sn and As among the temper brittleness temperature zones clustering at the original austenite crystal boundary to form brittle thin layer and seriously lowering the coagulating strength at crystal boundary. The concentration of alloy elements Mn and Cr at the crystal boundary helps to strengthen the sensitivity of the steel to temper brittleness.

Experiments in our laboratory show that when a small quantity of Mo (less than 2.5%) is added in solid solution to the carbonless Fe-Ni-Mn maraging steel, the temper brittleness cannot be noticeably vanished. The result is shown in Figure 9. But if a considerable amount of Mo and Ti is added to maraging steel so as to guarantee a precipitation of great amount of hexagonal close-packed phases, Ni_3Mo, Ni_3Ti and reversed austenite, after a treatment of normal aging. Then the temper brittleness can be basically vanished and a combination of high strength and high toughness will come out (see Figure 1). 12Ni maraging steel, in which Mn and Cr are used to partially replace Ni and Co, as studied in this article, after a treatment of low temperature and short-time aging, can have a certain degree of temper brittleness. The result is shown in Figure 10. But, as mentioned above, after a treatment of normal aging and great amount hexagonal close-packed phases Ni_3Mo and Ni_3Ti have been precipitated out, the temper brittleness will disappear and the crack toughness will be improved. It becomes obvious that although in steel the existence of a small amount of such elements as Sb, P, As and Sn, which can cause temper brittleness, is inevitable, through a reasonable system of alloying and heat treatment, it is still possible to have aging work and precipiation phases that can block the forming of brittleness state and temper brittleness can be avoided or eleminated.
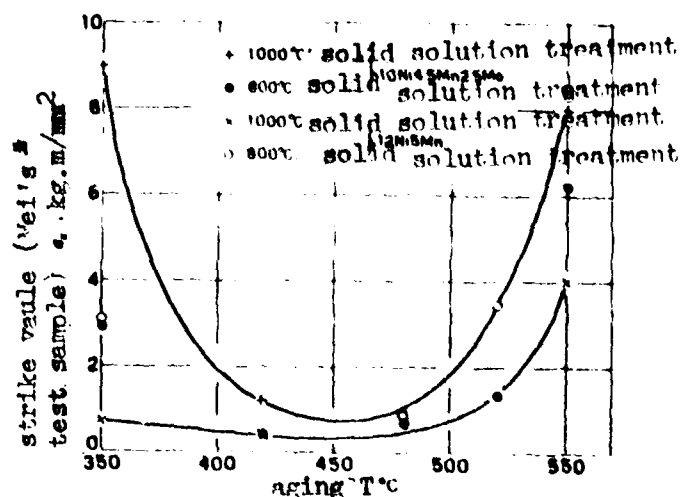
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Figure 9 The action of temper brittleness when a small amount of Mo
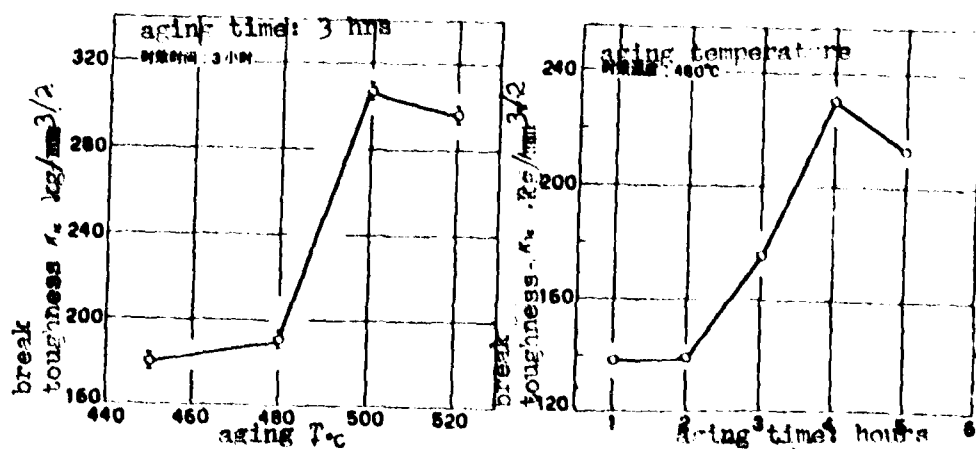(solid solution state) is added to Fe-Ni-Mn maraging steel

Figure 10   The effect of aging temperature and aging time to the
toughness of 12Ni4Co3Cr1.5Mn maraging steel

The phenomenon that the hexagonal close-packed phases, Ni_3Mo, Ni_3Ti and

reversed austenite can noticeably eleminate temper brittleness, is a subject

worthy of further studies.

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* A transliteration of Ch'nese.

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6. Conclusions

(1) According to the method of using average electron hole number or average electron concentration successfully to predict the stability and solubility of high temperature austenite in the study of high temperature alloy, we suggest an electron concentration criterion which can be applied to maraging steel as follows:

$$N_{\cdot \mu} = 7.75 + 0.10\left(\frac{1200 - T}{100}\right)$$

Here T stands for Celsius's temperature. Based on this, we would like to point out the possibility and limitation of reducing Ni and Co contents in maraging steels.

(2) Our observation in experiments has evidenced the characteristics of easy cross-slip behavior of the dislocation lines in maraging steels. Because in the matrix of body-centred cubic martensite, the cross-slip of tilted dislocations left no press-bar dislocation, the addition of Co, which can lower fault energy, will not obstruct cross-slip.

(3) Our experiments show that Mn, Cr and Co can all lower fault energy, but their action of stabilising dislocation lines and action to hypocrystal structure are different.

(4) Our experiments show that the aging precipitation phases of 12 Ni maraging steel which contains Mn and Cr and with low contents of Ni and Co are similar with the phases of 18Ni9Co maraging steel. The main phases are Ni_3Ti (greatest amount), Ni_3Mo and reversed austenite and some location contains a small quantity of δ-FeMo phase. The orientation of the bar-like

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or band-like precipitation phase of Ni_3Ti along four $\langle 111 \rangle$ directions forms zigzag space-lattice structure and very effectively entwines the dislocation lines of easy cross-slip. So there is a gain of higher strengthening effect ($\sigma_b = 180kg/mm^2$) and a toughness reaches the level of 18Ni9Co steel ($K_{1c} = 320-400$ kg.mm$^{-3/2}$).

(5) We discussed the hexagonal close-packed fault layer nucleated on dislocation lines from the hexagonal close-packed phases, Ni_3Mo and Ni_3Ti in maraging steel, which was suggested in our previous article[1]. By this, a few phenomena in our experiments can be explained, and at the same time we discussed the relationship between the separation of hexagonal close-packed precipitation phases and temper brittleness.

In short, the result of our study of maraging steels which contain Mn and Cr and with lower contents of Ni and Co, provides a useful view of the possibility of reducing the contents of Ni and Co in maraging steels.

Bibliography

(1) Tsai Chi-kung, Chu Ching and Ho Chung-chih, Acta Physica Sinica, 23 (1974),178.
(2) Steinen, A. and Schuben, F., DEW-Tech. Ber., 6 (1960).
(3) Srawlay, J.E. and Brown, W.F., Plane Strain Crack Toughness Testing of High Strength Metallic Materials, Amer.Soc. Test. Mater., Tech.Publ., No. 410, (1966), PP.1-65.
(4) Patterson, R.L. and Wayman, C.M., Acta Met., 14 (1966), 347.
(5) Banerjee, B. R. et al., Metal Sci. J., 2 (1968), 77.
(6) Detert, K., Trans. AIME, 239 (1967),553.
(7) Squires, D. R. and Wilson, E.A., Met. Trans., 3 (1972), 575.

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